Thermoelectric effects in correlated quantum dots and molecules

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Abstract. We investigate thermoelectric properties of correlated quantum dots and molecules, described by a single level Anderson model coupled to conduction electron leads, by using Wilson's numerical renormalization group method. In the Kondo regime, the thermopower, $S(T)$, exhibits two sign changes, at temperatures $T = T_1$ and $T = T_2 > T_1$. We find that T_2 is of order the level width Γ and $T_1 > T_p \approx T_K$, where T_p is the position of the Kondo induced peak in the thermopower and T_K is the Kondo scale. No sign change is found outside the Kondo regime, or, for weak correlations, making a sign change in $S(T)$ a particularly sensitive signature of strong correlations and Kondo physics. For molecules, we investigate the effect of screening by conduction electrons on the thermoelectric transport. We find that a large screening interaction enhances the figure of merit in the Kondo and mixed valence regimes.

1. Introduction

Materials with high thermoelectric efficiency are currently under intense theoretical and experimental investigation, largely due to the prospect of applications, e.g., for the conversion of waste heat into electricity, or for refrigeration and on-chip cooling in microelectronics [1, 2]. Apart from applications, thermoelectric materials also serve as an interesting testing ground for new theoretical approaches to thermoelectric transport in solids[3, 4, 5]. Coulomb correlations and the Kondo effect give rise to large thermoelectric coefficients in strongly correlated bulk materials [6, 7, 8, 9]. They are also important in nanoscale semiconducting devices and in molecular transistors, posing interesting theoretical and experimental challenges for the understanding of electrical and thermal transport in such systems[10, 11, 12, 13, 14, 15, 16].

In this paper we address the thermoelectric properties of two related systems: a nanoscale size quantum dot exhibiting the Kondo effect, which we describe in terms of a single level Anderson impurity model with two conduction electron leads at fixed chemical potentials, and, a molecular transistor described by an extension of the above model to include a local screening of the Coulomb interaction on the molecule by the electrons in the leads. The quantum dots or molecules that we consider can be tuned from the Kondo to the mixed valence and empty orbital regimes by a gate voltage [17, 18]. Very recent experiments on nanoscale quantum dots [10] are beginning to probe the effect of Kondo correlations on the thermopower.

We use Wilson's numerical renormalization group (NRG) method [19, 20] to calculate the linear conductance, thermopower and thermal conductance as a function of temperature and gate voltage. The technique gives reliable results for transport properties in all regimes of

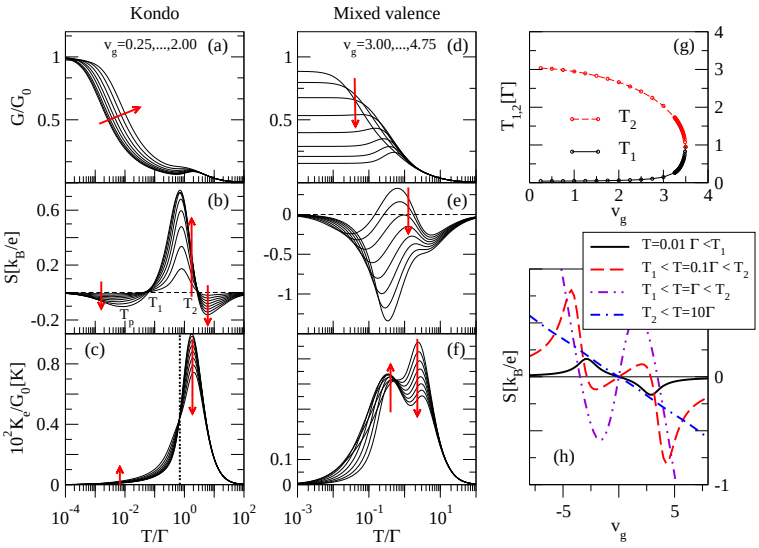

Figure 1. Conductance, G, thermopower, S, and, thermal conductance, K_e, versus T/Γ, for $U = 4\Gamma = 0.08$ and gate voltages, $v_g = (\varepsilon_d + U/2)/\Gamma$, in the Kondo (a-c) and mixed valence (d-f) regimes ($G_0 = 2e^2/h$). The v_g are indicated in top panels and increase by 0.25. Arrows show trends with increasing v_g. T_p: position of low temperature peak in S. Temperatures $T_{1,2}$ at which $S(T)$ changes sign are shown in (g) versus v_g. (h): gate voltage dependence of S at representative temperatures T relative to $T_1(0)$ and $T_2(0)$.

interest[4]. The recently introduced full density matrix (FDM) approach [21](see also [22]) is used. This allows calculations of dynamical properties at all excitation energies ω relative to the temperature T, thereby simplifying the calculation of transport properties which require knowledge of excitations, ω, above and below the temperature.

2. Model and transport properties

We describe both the nanoscale quantum dot and the molecular transistor by the single level Anderson impurity model with two conduction electron leads

$$H = \sum_{\alpha k\sigma} \epsilon_{\alpha k\sigma} c^\dagger_{\alpha k\sigma} c_{\alpha k\sigma} + \sum_\sigma \varepsilon_d\, d^\dagger_\sigma d_\sigma + U n_{d\uparrow} n_{d\downarrow} + H_{\rm screening} + \sum_{\alpha k\sigma} t_\alpha (c^\dagger_{\alpha k\sigma} d_\sigma + h.c.). \quad (1)$$

Here, $\epsilon_{\alpha k\sigma}$ is the kinetic energy of electrons with wavenumber k and spin σ in lead $\alpha = (L, R)$, ε_d is the local level energy, U is the local Coulomb repulsion and t_α is the tunnel matrix element of the local level to conduction electron states in lead $\alpha = (L, R)$. $H_{\rm screening} = U_{dc}(n_d - 1)(n_0 - 1)$, with n_d the local level occupancy and n_0 the local occupancy of the lead electrons, represents the screening interaction for the case of the molecule. We assume symmetric couplings of the dot to both leads and use the full width at half maximum, $\Gamma = 0.02$, as the energy unit throughout.

Thermoelectric transport is calculated for a situation in which a small external bias voltage, $\delta V = V_L - V_R$, and a small temperature gradient δT is applied between left and right leads following [11, 12]. To linear order, the following expressions for the electrical conductance, $G(T)$, the thermal conductance, $K_e(T)$, and the thermoelectric power, $S(T)$, are obtained

$$G(T) = e^2 I_0(T) \quad (2)$$

$$S(T) = -\frac{1}{|e|T}\frac{I_1(T)}{I_0(T)} \quad (3)$$

$$K_e(T) = \frac{1}{T}\left[I_2(T) - \frac{I_1^2(T)}{I_0(T)}\right] \quad (4)$$

where $I_n, n = 0, 1, 2$ are the transport integrals

$$I_n(T) = \frac{2}{h}\int d\omega\, \omega^n \mathcal{T}(\omega)(-\frac{\partial f}{\partial \omega}). \quad (5)$$

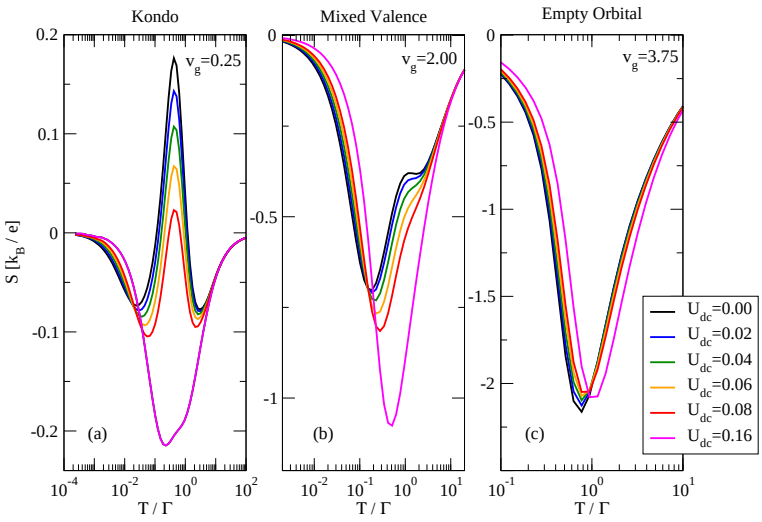

Figure 2. Temperature dependence of the thermopower, $S(T)$, for $U = 4\Gamma = 0.08$ in the Kondo, (a), mixed valence, (b), and empty orbital, (c), regimes for increasing values of the screening interaction U_{dc}. The case of large screening $U_{dc} = 0.16 > U$ is qualitatively similar to a large local electron-phonon coupling and results in destruction of Kondo correlations at finite gate voltages. Screening has a negligible effect in the empty orbital regime, but affects significantly $S(T)$ in the other regimes.

Here, e denotes the magnitude of the electronic charge and h denotes Planck's constant. The transmission function $\mathcal{T}(\omega) = \pi\Gamma A(\omega)$, where $A(\omega)$ is the d-level spectral density.

3. Results for quantum dots: $U_{dc} = 0$

The temperature dependence of the electrical conductance, $G(T)$, thermopower, $S(T)$, and electronic part of the thermal conductance, $K_e(T)$, are shown in Fig. 1a-c in the Kondo regime and in Fig. 1d-f in the mixed valence regime [23]. The thermopower exhibits two sign changes in the Kondo regime at $T = T_1(v_g)$ and $T = T_2(v_g)$ and no sign changes on entering the mixed valence regime (see Fig. 1e). The gate voltage dependence of S in Fig. 1h shows three characteristic types of behaviour depending on the T relative to $T_1(0)$ as explained in [23].

4. Results for molecules: $U_{dc} \geq 0$

For molecules in metallic break junctions, we expect additional effects to be important for thermoelectric properties, e.g. local phonon modes and screening by the conduction electrons in the leads. Here, we investigate the effect of the latter, and note that the effect of a strong local electron-phonon coupling can be approximately simulated by choosing a large screening interaction $U_{dc} > U$.

For moderate screening interactions $U_{dc} < U$, we recover the expected downward renormalization of the local Coulomb repulsion $U \to U^* < U$ and an upward excitonic renormalization of the effective hybridization with increasing U_{dc} leading to a weakening of Kondo correlations. Correspondingly, transport properties are significantly affected in the Kondo and mixed valence regimes, as shown in Fig. 2 for the thermopower and in Fig. 3 for the figure of merit. For large screening interactions $U_{dc} > U$ we find a destruction of Kondo correlations for gate voltages $v_g > 0$ away from particle-hole symmetry with an enhancement of the figure of merit for "Kondo" and "mixed valence" regimes (referred to the $U_{dc} = 0$ case).

5. Conclusions

The thermoelectric power of, (i), quantum dots, and, (ii), molecules in break junctions, has been investigated using a single-level Anderson model. We showed that the thermopower exhibits sign changes as a function of temperature and gate voltage. These can be used as sensitive probes of Kondo correlations. Recent measurements on Kondo correlated quantum dots [10] are in qualitative agreement with our model calculations [23]. The effect of lead electron screening on

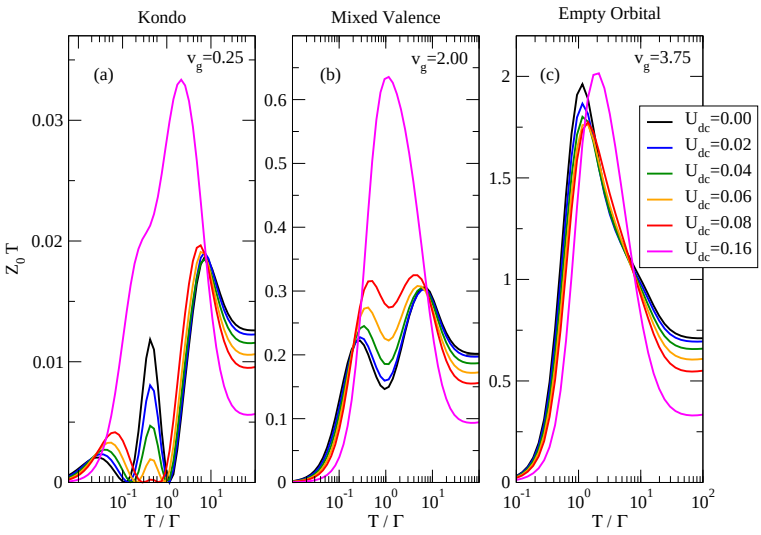

Figure 3. Temperature dependence of the "figure of merit" $Z_0T = GS^2T/K_\mathrm{e}$ for $U = 4\Gamma = 0.08$ and increasing values of the screening interaction U_{dc} in different regimes (by reference to the $U_{dc} = 0$ case). The true figure of merit $ZT = GS^2T/(K_\mathrm{e} + K_\mathrm{ph})$ includes a material specific phonon contribution, K_ph, which we have neglected, but needs to be included whenever phonons dominate thermal transport. Provided all scales are less than the Debye temperature θ_D, we expect that $ZT \approx Z_0T$.

molecular transport is shown to be significant in the Kondo and mixed valence regimes, where we find that an enhanced figure of merit can result. In future, it would be interesting to include a local electron-phonon coupling of the molecular state in order to investigate the effect of this interaction on molecular transport in detail[24].

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